PROPOSAL FOR TOPIC APPROVAL TO BE SUBMITTED TO THE UNIVERSITY OF MUMBAI FOR THE Ph. D. DEGREE IN THE SUBJECT OF CHEMISTRY

Title of the topic	:	Design of graphene-based Carbon Nanomaterials for the separation of actinides and lanthanides from spent nuclear fuel: Density Functional Theory Simulations
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TITLE

Design of graphene-based Carbon Nanomaterials for the separation of actinides and lanthanides from spent nuclear fuel: Density Functional Theory Simulations

AIMS OF THE STUDY

This study aims to utilize the tools of Computational Chemistry and Density Functional Theory (DFT) simulations to

1. Design novel carbon nanomaterials for the purpose of separation of actinides and lanthanides
2. Investigate the binding interaction of the nitrides, chlorides and fluorides of various lanthanides and actinides with the carbon-based substrate materials
3. Functionalize substrates with the intent of enhancing binding performance towards the lanthanides and actinides

OBJECTIVES OF THE STUDY

The objective of this work is to investigate the binding interactions of actinides, especially U, Pu, Am, Np in nitride, chloride and fluoride form with carbon nanostructures like graphene and graphdiyne. Functionalization of the carbon nanostructures with different ligands with the aim to increase solubility will also be explored. The performance of the optimized systems will be assessed and compared using the binding energy of interaction between the actinide and ligands present over graphyne/graphdiyne. To assess the practical feasibility of these materials, the weight percentage of the Actinides / Lanthanide bound on carbon nano-structure surface will be computed. Further, to assess the stability of the optimized system at ambient temperatures or higher temperatures, ab initio Molecular Dynamics simulations will be conducted. Sorption capability will be evaluated by computing thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (H), entropy (S), adsorption energy, interaction energy, and deformation energy. Insights into the binding mechanism through band structure analysis, the density of states analysis and charge transfer analysis will be carried out. This study will allow for the

identification of materials that can bind effectively with Actinides or Lanthanides and ways to streamline these materials to maximize their performance.

STUDY BACKGROUND (LITERATURE REVIEW) AND SIGNIFICANCE OF STUDY

Currently, nuclear power accounts for approximately 11% of all the electricity generated worldwide. There are 434 nuclear power plants currently in operation in 30 countries. Management of spent nuclear fuel is thus an important issue that will increase in relevance if nuclear power becomes more widely adopted internationally. The two long-term options for the management of spent nuclear fuel are (1) storage in a deep geological repository or (2) separation and recycling of the actinide elements. The spent fuel mainly contains isotopes from the Actinides and Lanthanide series. Approx. 95% of spent nuclear fuel consists of uranium (U) and plutonium (Pu), which can be separated from the remainder of the spent fuel and subsequently converted into a Mixed Oxide (MOX) material that can be recycled as fuel.[1]

A variety of chemical methods have been proposed and demonstrated for reprocessing spent fuel. Solids are seldom analyzed as such for actinides but are generally dissolved so that standard analysis methods for liquids can be applied. The two most widely implemented and investigated methods are referred to as aqueous reprocessing and pyroprocessing. The classical process to recover uranium (U) and plutonium (Pu) from used nuclear fuel using tributyl phosphate (TBP), namely the Plutonium Uranium Redox EXtraction (PUREX) process. Pyroprocessing utilizes molten salt electrolytes as the media rather than acidic aqueous solutions and organic solvents. The extractant, tributyl phosphate, used in the PUREX process are toxic whereas pyroprocessing requires structural materials that can withstand the high temperatures and the corrosive molten salts.[2] Therefore, there is a need for establishing recycling processes that involve non-toxic materials. In this work, novel 2D carbon-based nanomaterials will be devised for application as substrate materials for pyroprocessing, and various avenues for tuning their performance will also be explored using DFT simulations to provide experimentalists with exhaustive theoretical calculations and predictions for potent materials that can be developed for this application.

NATIONAL STATUS

Adoption of the closed nuclear fuel cycle is an imperative option for the Indian nuclear power programme given the limited resources of natural uranium and abundance of thorium. The issues associated with the long-term radiotoxicity of spent fuel can also be addressed in the closed fuel cycle with this option. Rajamani Natarajan paper focuses on the scientific and technological challenges associated with reprocessing spent fuel from both thermal and fast reactors. The experience gained in the operation of reprocessing plants in the separation of spent fuel of thermal reactors into uranium, plutonium and high-level waste is described.[10]

INTERNATIONAL STATUS

Since entering a new era of globalization, the nuclear power industry is undergoing a huge revolution. Although the nuclear industry can provide large-scale stable energy and effectively reduce carbon dioxide, the development of nuclear power is still highly controversial. One of the most important reasons is that radioactive waste will be generated around the utilization of nuclear energy. Uranium and plutonium ions and their complexes play an important role in nuclear fuel reprocessing, and their trace characterization is important in nuclear forensics. Kumar et al perform ab initio density functional theory calculations of U and Pu complexes with graphene and graphene oxide to examine the applicability of a graphene-based fissile sensor. They also found that graphene needs to be functionalized to act as an effective sensor for the detection of fissile materials such as uranium and plutonium complexes.[11]

Lewis et al reported a promising new class of highly selective solvent extraction reagents for the partitioning of trivalent actinides from trivalent lanthanides in nuclear waste streams and have demonstrated that preorganization of the donor atoms for metal ligation with a rigid cis locked 1,10-phenanthroline motif leads to a rapid and highly efficient separation of actinides from lanthanides.[12]

STUDY HYPOTHESES

1. This study hypothesizes that 2D carbon nanomaterials can be efficient substrates for binding with lanthanides and actinides, allowing for their use as substrates in the pyroprocessing of spent nuclear fuel.
2. Further, the use of 2D carbon nanomaterials in this manner can present a non-toxic, eco-friendly and cost-effective strategy for recycling spent nuclear fuel.

3. The performance of these materials can be tuned by functionalization using functional groups or forming heterostructures, by introducing defects, or by any combination/s of these.
4. Density Functional Theory Simulations present a rapid technique for investigation of binding interactions between the substrate and analyte, and can be useful for the prediction of suitable materials that can effectively replace the toxic materials used in pyroprocessing methods.

STUDY RATIONALE

In the past few years, carbon nanostructures like carbon nanotubes, graphene, and their functionalized structures have become an interesting field of study in the treatment of nuclear waste management because of their unique structure and physicochemical properties.[3] Among recently prepared carbon nanomaterials, graphene oxide (GO) has been widely used as a highly efficient adsorbent to remove environmental pollutants because of the numerous oxygen-containing functional groups such as -OH and -O- groups located on basal planes and -COOH groups at nanosheet edges. Incorporation with other functional materials could enhance the GO performance. Further, it was found that the polyaniline modified graphene oxide has an exceptional ability to selectively extract U(VI) from aqueous solutions.[4] Graphdiyne (GDY), has unique electrical and conductive properties. In its 2D form, graphdiyne can chemically combine with actinyl species, directly reducing actinide contamination with the formed GDY-actinyl complexes showing potential as catalysts in various reactions.[5] Some theoretical work has also been reported that studies the interactions of graphene oxides with actinide complexes.[6,7] However, to the best of the author's knowledge- graphyne, graphdiyne, and their related structures have not been explored extensively for applications in the separation of nuclear waste materials. There may be a possibility of these structures binding with radionuclides and effectively producing better results.

RESEARCH METHODOLOGY

We will perform the geometry optimization of the host structures as well as the radioactive nuclides to obtain the minimum energy structure and frequencies. All the calculations will be carried out using DFT simulations.[8] The accuracy of DFT simulations rely heavily on the choice of the exchange-correlation functional. By taking into account the computational accuracy and consumption of resources, the Generalized Gradient Approximation (GGA)

method is currently recognized as the basic choice for the systems containing dozens of atoms.[9] Hybrid functionals, which contain a part of the Hartree-Fock exchange, may give better results in the complexes formed by actinides/lanthanides. System performance will be evaluated making use of different functionals to assess the extent of sensitivity of results on the choice of the exchange-correlation functional. The changes in the property upon functionalization with various functional groups will be explored. The materials showing promise in terms of binding interactions with the chlorides, fluorides and nitrides of various lanthanides and actinides will be further investigated for the mechanism of the interactions. The practical feasibility of the materials will be explored using ab initio Molecular Dynamics (MD) simulations, and other suitable calculations.

STATISTICAL PLAN

DFT simulations involve solving the Schrodinger equation using trial functions of the electron's probability distribution function, in a set of electronic followed by ionic iterations. The solution is arrived at by means of an iterative, self-consistent procedure wherein the output of the previous iteration serves as the input for the next iteration, and this cyclic procedure is continued until certain criteria for convergence of the structure are met. These criteria, namely an upper limit to the Hellman-Feynman forces and energy difference between two consecutive iterations are set before running the simulations depending on the system at hand. Further, parameters like the K-point grid size that should be used for sampling the Brillouin Zone, number of iterations, energy cut-off, etc., also are set depending on the system. Trial runs are required to identify suitable values of these parameters.

The results of DFT simulations are affected by the choice of the exchange-correlation functional. The most commonly used functionals are the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). The LDA assumes the electron density in the form of a homogenous electron cloud, which may overestimate binding interactions in some cases. On the other hand, GGA considers a gradient of electron density which can underestimate binding interactions, especially long-range dispersion interactions. These can be corrected by means of many available dispersion correction schemes like Grimme's DFT D2, DFT-D3, Tkachenko-Scheffler (TS) Scheme, etc. Hybrid functionals containing part of the actual Hartree-Fock exchange interaction are sometimes found to be more accurate for certain

systems. In this study, a range of functionals will be tested for the systems, and the extent of sensitivity of the results to this choice of exchange-correlation functionals will be assessed.

LIMITATIONS OF THE STUDY

This study uses theoretical and computational tools to predict suitable substrate material replacements for the pyroprocessing of spent nuclear fuel. These predictions may not be completely achieved in practicality, as all variables, in reality, cannot be simulated computationally. Further, the materials predicted in this study can be employed for the application widely if its fabrication method is facile and inexpensive. Extensive studies will be needed to arrive at good synthesis strategies that can be scaled up for these fabrication processes. DFT simulations are carried out at zero Kelvin, therefore system performance at higher or ambient temperatures may vary, as will system stability. This limitation will be addressed by performing ab initio MD simulations to check for system integrity at ambient temperatures.

EXPECTED OUTCOMES OF THE STUDY

The present scheme mainly proposes a non-toxic noble carbon nanostructure-based extractant for the separation of actinides from spent fuel. The study will cover theoretical aspects of ligands to increase the solubility of graphyne and graphdiyne in an aqueous environment. The advancement of theoretical studies in this direction will provide the experimentalist detailed input and procedure for practical implementation of noble carbon nanostructure for efficient and effective separation of actinides/lanthanide from spent fuel.

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